Leaching of rare earths from bauxite residue (red mud)

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ABSTRACT

Bauxite residue (or red mud) is a waste generated during the Bayer process of alumina production. Its storage is a spatial and environmental concern. Currently, there are no bulk applications of bauxite residue except for minor use in cements and ceramics. Nonetheless, some types of bauxite residues are rich in rare-earth elements (REEs), and the extraction of scandium in particular is of special interest. Leaching experiments on Greek bauxite residue were performed with different acids at different concentrations, liquid-to-solid ratios, leaching times and temperatures. Extraction of the REEs was high for leaching in HCl solutions compared to other acids, but the dissolution of iron was high as well (~60%). The maximum extraction of the REEs was around 80%. Sodium and calcium were completely dissolved during leaching. Dissolution of aluminum, silicon and titanium was between 30% and 50%. The leaching data show a very close association of scandium with the iron oxide phases.

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1. Introduction

Bauxite is the major ore for aluminum production. Alumina is extracted from bauxite by the Bayer process. The waste slurry generated in this process is called red mud and its solid fraction is called bauxite residue. About 1–2 metric tonnes of bauxite residue is generated for each tonne of alumina produced (Kumar et al., 2006). The global annual generation of bauxite residue is around 120 million tonnes and 2.7 billion tonnes of this material has already been stockpiled (Klauber et al., 2011). The pH of the wet red mud slurry is about 12. It is stored in huge tailing ponds and this poses a significant problem, since it not only occupies vast land areas, but it can also lead to environmental pollution (Power et al., 2011). Hence, there is a need for better management strategies (preferably utilization) of the bauxite residue. However, currently there are not many large-volume applications of bauxite residue besides minor use in cement and ceramic production (Binnemans et al., 2013; Klauber et al., 2011; Kumar et al., 2006; Pontikes and Angelopoulos, 2013). Nonetheless, bauxite residue contains several interesting minor or trace elements, among which the rare-earth elements (REEs). More than 90% of the trace metal value in bauxite residue can be attributed to the presence of one of these REEs, namely scandium (Binnemans et al., 2013). Considering the revived interest on REEs due to supply concerns, novel research in the area is likely to take place.

Bauxite ores are classified in three different ways based on: (1) genetic principles: (1a) bauxites on igneous and metamorphic rocks; (1b) bauxites on sediments: carbonate rocks and clastic strata; (2) geological age: (2a) Palaeozoic; (2b) Mesozoic; (2c) Cenozoic; and (3) mineralogical composition: (3a) gibbsite bauxites; (3b) boehmite bauxites; (3c) diasporic bauxites (Valette, 1972). The bauxites on carbonate rocks (karst) have higher REE concentrations compared to other bauxites (Mordberg, 1993). Karst bauxites are mainly located in Europe, Jamaica, Russia and China. These bauxites account for 14% of total bauxite reserves (Bárdsossy, 1982). The REEs report to bauxite residue in the Bayer process. The enrichment factor of the REEs in bauxite residue compared to bauxite is about two (Ochsenkühn-Petropulu et al., 1994). REEs are present in bauxite as mineral phases or as ions that are either absorbed on the surface of minerals or replacing similar ions in the lattice of some matrix minerals (Li et al., 2013).

Some literature data on the leaching of REEs from bauxite residue are available (Fulford et al., 1991; Ochsenkühn-Petropulu et al., 1996; Ochsenkühn-Petropoulou et al., 2002; Qu and Lian, 2013; Smirnov and Molchanova, 1997; Wang et al., 2011, 2013; Xue et al., 2010; Yatsenko and Pyagai, 2010; Zhang et al., 2005). Fulford et al. (1991) developed a process for the extraction of REEs from Jamaican bauxite residue using sulfur dioxide, whereby REEs are selectively dissolved while leaving iron and titanium substantially undissolved in the bauxite residue. Ochsenkühn-Petropulu et al.
compared metal leaching extraction with different acids, different acid concentrations and different leaching conditions. Their results showed that 0.5 N HNO₃ leaching at 25 °C for 24 h with a liquid-to-solid (L/S) ratio of 50:1 recovered 80% of scandium, 90% of yttrium, 70% of the heavy lanthanides (Dy, Er, Yb), 50% of the middle ones (Nd, Sm, Eu, Gd) and 30% of the light lanthanides (La, Ce, Pr). The leaching process with dilute HNO₃ was performed at pilot scale and optimized for the extraction of scandium from bauxite residue (Ochsenkühn-Petropoulou et al., 2002). Xue et al. (2010) found that at a reaction temperature of 90 °C and an L/S ratio of 3:1, over 80% of the scandium in bauxite residue could be leached by H₂SO₄. Zhang et al. (2005) recovered 80% of scandium by HCl leaching at acid concentration of 6 mol/L HCl, L/S ratio of 4:1, temperature of 50 °C and a reaction time of 1 h. Wang et al. (2010) studied the extraction of scandium from bauxite residue by using HCl as leaching agent, with an L/S ratio of 5:1, an acid concentration of 6 mol/L, a reaction temperature of 50 °C and a reaction time of 1 h. Qu and Lian (2013) leached REEs and radioactive elements from bauxite residue by bioleaching.

The majority of the literature studies focus upon scandium and very little on other REEs. Neither has much work been done on leaching of major elements from bauxite residue nor leaching of REEs by organic acids. Study on the leaching of major elements is, however, useful for the development of the further purification process. Therefore, in this study we systematically investigated the extraction of REEs as well as other major elements in organic and mineral acids (HCl, HNO₃, H₂SO₄, CH₃COOH, CH₃SO₄H and citric acid). The effect of different parameters such as acid type and concentration, leaching time, liquid-to-solid ratio and temperature were investigated.

3. Results and discussion

3.1. Characterisation of the bauxite residue

The concentrations of the major elements in the form of oxides in Greek bauxite residue is given in Table 1. Iron oxide is the major oxide in the bauxite residue followed by alumina, silica, calcium oxide, titanium oxide and sodium oxide. The concentrations of the REEs is given in Table 2. The relative standard deviation was less than 20%. From the table, it is evident that the bauxite residue sample is richer in light REEs than in heavy REEs. It is also rich in scandium (121 g/tonne). The total REE concentration is around 0.1 wt%.

The following major minerals and compounds were identified by X-ray powder diffraction (XRD): the iron minerals hematite and goethite; the aluminum minerals gibbsite and diaspore; the calcium mineral calcite and the sodium compound cancrinite (Fig. 1). TGA–DSC curves of the bauxite residue show three slopes (TGA) and three peaks (DSC) (Fig. 2). The weight loss between 300 and 600 °C is due to decomposition of hydroxides in different

<table>
<thead>
<tr>
<th>Compound</th>
<th>wt%</th>
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<tbody>
<tr>
<td>Fe₂O₃</td>
<td>44.6</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>23.6</td>
</tr>
<tr>
<td>CaO</td>
<td>11.2</td>
</tr>
<tr>
<td>SiO₂</td>
<td>10.2</td>
</tr>
<tr>
<td>TiO₂</td>
<td>5.7</td>
</tr>
<tr>
<td>Na₂O</td>
<td>2.5</td>
</tr>
</tbody>
</table>

Table 2

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration (g/tonne)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc</td>
<td>121 ± 10</td>
</tr>
<tr>
<td>Y</td>
<td>75.7 ± 9.6</td>
</tr>
<tr>
<td>La</td>
<td>114 ± 15</td>
</tr>
<tr>
<td>Ce</td>
<td>368 ± 68</td>
</tr>
<tr>
<td>Pr</td>
<td>280.0 ± 3.9</td>
</tr>
<tr>
<td>Nd</td>
<td>98.6 ± 7.0</td>
</tr>
<tr>
<td>Sm</td>
<td>21.3 ± 2.3</td>
</tr>
<tr>
<td>Eu</td>
<td>5.0 ± 0.9</td>
</tr>
<tr>
<td>Gd</td>
<td>22.0 ± 1.9</td>
</tr>
<tr>
<td>Tb</td>
<td>3.5 ± 0.6</td>
</tr>
<tr>
<td>Dy</td>
<td>16.7 ± 0.7</td>
</tr>
<tr>
<td>Ho</td>
<td>3.9 ± 0.6</td>
</tr>
<tr>
<td>Er</td>
<td>13.5 ± 1.8</td>
</tr>
<tr>
<td>Tm</td>
<td>1.9 ± 0.3</td>
</tr>
<tr>
<td>Yb</td>
<td>14.0 ± 1.9</td>
</tr>
<tr>
<td>Lu</td>
<td>2.4 ± 0.3</td>
</tr>
</tbody>
</table>

The leaching of the bauxite residue was carried out in sealed polyethylene bottles by constant agitation using a laboratory shaker (Gerhardt Laboshake) at 160 rpm and 25 °C. High-temperature leaching experiments were carried out in a 500 mL glass reactor fitted with a reflux condenser and placed on a temperature-controlled ceramic hot plate with a magnetic stirring system. The leach solution sample was filtered using a syringe filter (pore size of 0.45 µm) and diluted with distilled water for ICP-MS analysis. Leaching experiments were repeated twice to assess the reproducibility and the error found was within the 10% range.

2. Experimental

The bauxite residue studied in this work was provided by the Aluminium of Greece, which is located at Agios Nikolaos, Greece. It originated from the mixture of karst and lateritic bauxites and is similar to the bauxite residue examined by Ochsenkühn-Petropoulou et al. (1994). It was received from the alumina refinery after dewatering by filter presses and room temperature drying. The sample was further dried at 105 °C for 12 h. Next, the material was passed through a 500 µm size mesh before it was used in leaching studies. Analytical reagent grade nitric acid (65%) (Chem-lab), sulfuric acid (99.6%) (Acros Organics) and methanesulfonic acid (98%) (Acros Organics) were used in the present study. Chemical analysis of major elements in bauxite residue was performed using wavelength dispersive X-ray fluorescence spectroscopy (WDXRF, Panalytical PW2400). Chemical analysis of minor elements was performed after complete dissolution of bauxite residue by alkali fusion and acid digestion in a 1:1 (v/v) HCl solution, followed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS, Thermo Electron X Series) analysis. The alkali fusion was carried out by mixing 0.5 g of bauxite residue with 1.5 g of sodium carbonate and 1.5 g of sodium tetraborate decahydrate, followed by heating the mixture in a platinum crucible at 1100 °C for 30 min. The mineralogy of the samples was studied by X-ray diffraction technique (XRD, Philips PW1830). The powder morphology was investigated by scanning electron microscopy (SEM, Philips XL30). The particle size of the samples was measured by laser particle size analysis (Malvern Mastersizer 3000). Thermogravimetric analysis (TGA, Netzsch STA 409) experiments were carried out in nitrogen atmosphere from room temperature to 1000 °C at a heating rate of 10 °C/min.
stages (due to decomposition of gibbsite and goethite between 300 and 400°C and of diaspore between 400 and 600°C) (Agatzini-Leonardou et al., 2008). The weight loss between 600 and 800°C is due to the decomposition of calcium carbonate present in the sample.

The cumulative particle size distribution of the bauxite residue sample is shown in Fig. 3. In the bauxite residue, 90% of the particles are smaller than 10 µm and 50% of the particles are smaller than 0.06 µm. Scanning electron microscopy (SEM) was used to study the morphology of the sample. The SEM pictures show that the bauxite residue is a very fine material and that aggregates are formed (Fig. 4). These results are in line with the particle size analysis. Particles larger than 10 µm were also observed in the cross section of the sample. It was difficult to perform EDX analysis on the individual particles due to the interference by neighboring particles. However, some phases were identified by EDX analysis, such as aluminum hydroxide (gibbsite or diaspore), hematite, rutile, calcium carbonate, calcium titanate, sodium aluminosilicates. This confirms the results of XRD. It was impossible to identify the rare-earth mineral phases in the bauxite residue due to their low concentrations. Other authors experienced similar difficulties (e.g. Ochsenkühn-Petropulu et al., 1996).
3.2. Leaching with water

Leaching studies with water were carried out to study the change in pH of bauxite residue and the possibility of sodium hydroxide removal prior to acid leaching. Prior removal by water would be beneficial as this would reduce the amount of acid needed to merely neutralize the high pH. The experiments were conducted at two L/S ratios: 5:1 and 50:1. Even after four washing steps, the pH of the solution did not decrease, i.e. the pH remained stable at around 10. This is due to the buffering activity of alkaline solids that are present in the sample (Thornber and Binet, 1999). Fig. 5 shows the sodium removal from the bauxite residue by water washing at different L/S ratios. Around 10–15 wt% of the total sodium content was removed from the solution after four washing steps. This is also due to the fact that most of the sodium in the bauxite residue is in the form of insoluble aluminosilicates. It can be concluded that water washing is not very efficient in neutralizing...
the pH prior to acid leaching. Therefore, the leaching study was performed using the bauxite residue without a prior washing step.

3.3. Leaching with acids

3.3.1. Acids of low concentration

Experiments were conducted at low acid concentrations (<1 N) of different mineral and organic acids to study the effect on pH and on leaching of different elements. Fig. 6 shows the effect of acid concentration on the pH of the solution. From this figure, it is evident that with increase in the acid concentration, the pH is decreasing. The studied organic acids except methanesulfonic acid (CH$_3$SO$_3$H) are weak acids. Acetic acid (CH$_3$COOH) is weaker than citric acid.

The effect of nitric acid concentration on the leaching of major elements is shown in Fig. 7. Dissolution of Ca and Na is high even at pH values above 5. The dissolution of aluminum, silicon, titanium and iron is also increased with a decrease in pH and it reached a maximum when pH value is around 1. The dissolution of aluminum and silicon increased simultaneously. This is due to dissolution of aluminum and silicon from the sodium aluminosilicates.

Fig. 8 shows the effect of different acids and their concentrations on the leaching of REEs. Not all the REEs are shown in the figure for the sake of readability. Extraction of Sc, Y, La, Ce, Nd are shown as their concentrations are relatively high in bauxite residue. Dy is also shown because its concentration is the highest among the heavy REEs. Iron is indicated in the graph to illustrate the selectivity of leaching. Fig. 8 shows that the leaching of REEs is increasing with increasing acid concentration up to 0.25 N acid concentration. Initially, acid is consumed for neutralization and dissolution of aluminosilicates. Leaching of REEs and major elements is almost similar for all mineral acids and methanesulfonic acid. The degree of dissolution of REEs, iron and titanium is lower in citric acid and is the lowest in acetic acid. This is attributed to the higher pH of the citric acid and acetic acid solutions, compared to the pH obtained with mineral acid leaching. Dissolution of iron may be low (<5%) in the solution, but the iron concentration is very high (~300 ppm) compared to REEs (~9 ppm) due to its high concentration in the sample.

The percentage extraction is different for different REEs. This is due to the association of REEs with different minerals and their ionic radii (Ochsenkühn-Petropulu et al., 1996; Qu and Lian, 2013). For example, some of the cerium in the bauxite residue is present in the form of CeO$_2$ or bastnaesite ((Ce, La)CO$_3$F) (Li et al., 2013) and is difficult to leach. Scandium is present in the iron (III) oxide lattice (Brookins, 1988). Therefore, it is not completely soluble in the acid solutions unless iron is completely dissolved.
The extraction is high for Y, followed by Dy, Nd, Sc, La and Ce. This order is slightly changed depending on the type and concentration of the applied acid. The leaching order is matching with the results given in the literature (Ochsenkühn-Petropulu et al., 1994) for the similar material. However, the extraction is lower in the present study, especially for Sc and Y. The difference is as high as 20%. This may be due to a change in raw materials or process parameters that were used 20 years ago compared with the current conditions in the Bayer process.

3.3.2. Acids of high concentration

Experiments were conducted at high concentrations (>1 N) of acids for 24 h with varying L/S ratio. The results for hydrochloric acid leaching are shown in Fig. 9. It can be seen that an increase in the L/S ratio increases the extraction of elements from the bauxite residue. Extraction of the rare earths also increases with increasing acid concentration, as was already noted at acid concentrations <1 N. Extraction of Y, Nd and Dy is higher than 80%, while that of Sc, La and Ce is around 70–80% at acid concentration of 6 N. Iron dissolution is increased with increasing acid concentration.
from less than 5% at 0.5 N acid concentration to around 60% at 6 N acid concentration. Titanium dissolution increased to around 60% at 6 N acid concentration and \( \text{L/S} \) ratio of 50:1. The recoveries were higher for HCl leaching compared to HNO_3 at 6 N acid concentration and \( \text{L/S} \) ratio. An increase in temperature does increase the extraction of REEs substantially. Fig. 14 shows the effect of citric acid on leaching of Sc, Y, Ce and Fe at different temperatures. Extraction of REEs from bauxite residue with citric acid at temperatures above 90 °C is comparable with that of mineral acids at room temperature.

4. Conclusions

The bauxite residue sample was a very fine material, with 90 wt% of the material having a particle size of less than 10 μm. The main minerals observed in the bauxite residue were gibbsite, diaspore, hematite, calcite and cancrinite. The concentration of the rare-earth elements (REEs) in the studied bauxite residue was around 0.1 wt%. Water washing had a very low impact for decreasing the pH of the slurry and sodium content. REE recoveries were similar in all acids at low acid concentrations (<1 N), except for citric and acetic acid, which yielded lower recoveries. Initially, acid was consumed for the neutralization of the alkali and aluminosilicates. Extraction of REEs increased with acid concentration, time and \( \text{L/S} \) ratio. Extraction of the REEs was the highest for HCl leaching compared to other acids, but the iron leaching was also high (~60%). Around 70–80% of the REEs could be recovered from the bauxite residue using 6 N HCl leaching for 24 h duration at temperature of 25 °C. Most of the Na and Ca in the bauxite residue dissolved into the solution during leaching. Extraction of Al, Si and Ti was around 30–50%. Increasing the leaching temperature did not improve recoveries for mineral acids at 0.5 N, but it helped in the case of citric acid leaching: the REE leaching results for citric acid above 90 °C were comparable those for mineral acids at 25 °C. The leaching data show that scandium in bauxite residue is very closely associated with iron.

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